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(74) Agent: ZOMBECK, Alan; Patent Department - Mail C01232, Dow Coming Corporation, 2200 West Salzburg Road, Auburn, MI 48611 (US).

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(71) Applicants: DOW CORNING CORPORATION [US/US]; 2200 West Salzburg Road, Auburn, MI 48611 (US). EG TECHNOLOGY PARTNERS, L.P. [US/US]; 42 Industrial Way, Wilmington, MA 01887 (US).

(72) Inventors: SEIBEL, Lisa, M.; 7255 York Street, Dexter, MI 48130 (US). NANAVATI, Shrenik, M.; 5407 Trailridge Drive, Midland, MI 48642 (US). WYMAN, John, E.; 693 Emeril Court, Sanibel, FL 33957 (US). RANGWALLA, Imtiaz, J.; 1 Iron Gate Drive, Andover, MA 01810 (US).

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(54) Title: LAMINATE ADHESIVE HAVING BIS-SILANES, MULTIFUNCTIONAL ACRYLATES AND ETHYLENICALLY UNSATURATED ACIDS

(57) Abstract: A laminate structure made by coating at least one side of a substrate with a laminating adhesive, bringing a coated side of said substrate into contact with a second substrate to form a multi-layer film, and treating said multi-layer film with a free radical initiator, wherein said laminating adhesive is the reaction product of a multifunctional acrylate, a bis-silane, and an ethylenically unsaturated acid, optionally dissolved in a solvent.

# LAMINATE ADHESIVE HAVING BIS-SILANES, MULTIFUNCTIONAL ACRYLATES AND ETHYLENICALLY UNSATURATED ACIDS

## Field of the Invention

The invention relates to silicon containing laminates having barrier and adhesive properties which are useful in packaging applications.

## Background of the Invention

It is well known that coatings containing silane compounds, multifunctional acrylates and itaconic acid improve the gas, oil, and flavor barrier performance of organic polymer film substrates; see, for example, PCT/BE98/00008, the US equivalent of which is US Serial No. 09/341,255, filed July 15, 1999, as well as adhesive properties. Moreover, the adhesion of the coating to the film surface, as well as the improved barrier characteristics provided by the silane coating, are greatly enhanced by exposing the coated film to electron beam radiation.

These "barrier adhesives" represent a significant advance in the art. However, it has been observed that while the barrier properties of the prior art coatings are excellent in environments at relative humidities of 80% or less, their performance suffers significantly at relative humidities of 90% or more.

The present inventors have surprisingly discovered that the combination of a bis-silane, a multifunctional acrylate, an optional aminofunctional silane, and an ethylenically unsaturated acid, gives excellent gas barrier properties at low to moderate relative humidity values, as well as excellent gas barrier properties at very high relative humidity values of 90% or more. The key improvement is the addition of bis-silane, which results in excellent barrier at humidities of greater than 90%.

While other patents teach the combination of a mono or multifunctional acrylate with an aminofunctional silane, none teaches the addition of the ethylenically unsaturated acid with an acrylate and bis-silane to make a barrier adhesive. For example, U.S. Patent No. 5,368,941 teaches a deformable, abrasion-resistant coating formulated from at least one multi-functional

acrylate monomer, at least one aminofunctional silane, colloidal silica and at least one acrylate-terminated polyalkylene oxide, but does not teach the addition of an ethylenically unsaturated acid. The acrylate-terminated polyalkylene oxide helps prevent gelling of the coating composition during stripping and also imparts the composition with deformability, without sacrificing abrasion resistance.

Other useful barrier compositions are also described in U.S. Patent No. 5,215,822, which teaches a methanol solution of a vinyl benzyl amine silane (Dow Corning Corp. Z-6032), itaconic acid, and water; coating this solution on a corona treated low density polyethylene film, drying, and then subjecting the coated film to electron beam radiation to graft the coating to the film surface and further improve the barrier properties of the silane coating. However, while this coating gives excellent gas barrier properties at low to moderate relative humidity values, the gas permeability increases drastically at very high relative humidity values.

Also, U.S. Patent No. 5,434,007 teaches a silane resin coated on a plastic film, where the silane resin is composed of a monofunctional acrylate and an aminofunctional silane. The composition does not utilize a free radical cure, nor does it incorporate the ethylenically unsaturated acid.

U.S. Patent Nos. 5,260,350 and 5,374,483 relate to a silicone coating composition which, when cured on a solid substrate either by ultraviolet or electron beam radiation, provides a transparent abrasion resistant coating firmly adhered thereon. The silicone coating is prepared by reacting at least one multifunctional acrylate monomer with an amino-organofunctional silane, mixing the modified silane with at least one acrylic monomer and thereafter adding colloidal silica. Again however, neither of these compositions teach the addition of an ethylenically unsaturated acid to achieve barrier properties.

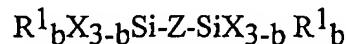
JP (Kokai) publication 7-18221 published on January 20, 1995 teaches a surface

treatment composition for gas barrier comprising an aminosilane and a compound having an aromatic ring or hydrogenated ring. The present invention is distinguishable, however, because it does not require the addition of cyclic compounds having an aromatic ring.

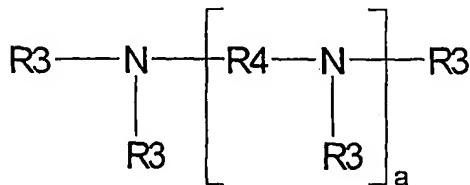
The present invention is distinguishable from the prior art because none teach the addition of a bis-silane to achieve improved gas barrier properties, or adhesive characteristics.

### Summary of the Invention

The invention is a method of laminating two substrates comprising coating at least one side of a substrate with a laminating adhesive, bringing a coated side of said substrate into contact with a second substrate to form a multi-layer film, and treating said multi-layer film with a free radical initiator, wherein said laminating adhesive is the reaction product of a multifunctional acrylate, a bis-silane, an optional aminofunctional silane, and an ethylenically unsaturated acid, optionally dissolved in a solvent, wherein the multifunctional acrylate has a molecular weight of from 100 to 3000, and the bis-silane has at least one molecule of the formula



wherein Z is  $R^2NH(R^2NH)pR^2$ , each  $R^1$  is a hydrocarbon group, each X is an alkoxy group with 1 to 4 carbon atoms, a halogen atom, an oxime group or an acyloxy group, each  $R^2$  is a divalent hydrocarbon group having 1 to 12 carbon atoms; b is from 0 to 3 and p is 0 or 1; and the optional aminofunctional silane has the formula



wherein a is 0-4, i.e.,  $0 \leq a \leq 4$ ;

$R^3$  is independently hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, arylalkyl,

acryl, methacryl, alkylaryl,  $R^4 - SiR_m(OR)_{3-m}$ , or an alkylene linking group having 2 to 12 carbon

atoms connected to one or two nitrogen atoms, with the proviso that at least one  $R^3$  is a hydrogen

atom and at most one  $R^3$  is an  $R^4 - SiR_m(OR)_{3-m}$  group, where m is 0, 1 or 2, and R is independently a hydrogen or an alkyl group having from 1 to 6 carbon atoms;  $R^4$  is independently

selected from the group consisting of linear or branched alkylene groups having from 1 to 12 carbon atoms; arylene groups having from 6 to 12 carbon atoms; and linear or branched hydrocarbon groups having from 1 to 16 carbon atoms and at least one alcohol, alcohol ether, ester,

amide, urea, thiourea or polyether group.

The laminate can be made from a variety of substrates. The laminate can then be used alone or with other substrates to give structural or barrier properties to packaging containers. The laminate adhesive can be further cured by drying in the presence of water prior to exposure to the free radical initiator. The free radical initiator can be electron beam irradiation, ultraviolet radiation, gamma radiation, and/or heat and chemical free radical initiators.

A laminate according to the present invention may be employed to provide a barrier which simultaneously adheres two substrates together and improves resistance of the material to transmission of gases and aromas therethrough. For example, a 30  $\mu m$  uncoated biaxially oriented, corona treated polypropylene film is generally found to have a permeability to oxygen of 1250cc/m<sup>2</sup>/day as measured at ASTM D3985-81 measured at 90% relative humidity. With the present coatings, the oxygen transmission rate of the same film can be reduced to less than

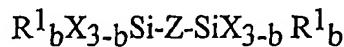
250cc/m<sup>2</sup>/day as measured at 90% relative humidity. As used herein, the terminology "improved barrier" refers to a laminate which can reduce oxygen transmission rate of the aforementioned uncoated polypropylene film from 1500 cc/m<sup>2</sup>/day to 250 cc/m<sup>2</sup>/day as measured at ASTM D3985-81 measured at 90% relative humidity.

### Description of the Preferred Embodiments

While the invention is susceptible of embodiment in many different forms there is described herein in detail preferred and alternate embodiments of the invention. It should be understood, however, that the present disclosure is to be considered an exemplification of the principles of the invention and is not intended to limit the spirit and scope of the invention and/or claims of the embodiments illustrated.

#### **Bis-silanes**

The key to the present invention is a bis-silane described by the general formula



wherein Z is  $R^2NH(R^2NH)_pR^2$ . In this formula each  $R^1$  is preferably a hydrocarbon group having 1 to 10 carbon atoms, for example a saturated or unsaturated aliphatic or aromatic group, for example alkyl alkenyl or phenyl groups; preferred groups are methyl and ethyl, the most preferred of which are methyl groups. Each X is an alkoxy group with 1 to 4 carbon atoms, a halogen atom, an oxime group or an acyloxy group, of these methoxy and ethoxy groups are preferred, the most preferred being methoxy groups.  $R^2$  may be a divalent hydrocarbon group having 1 to 12 carbon atoms, preferably each  $R^2$  has from 2 to 3 carbon atoms. Each b is from 0 to 3 but is most preferably 0, and p is 0 or 1. The best results are obtained by use of compounds in which each X is a methoxy group, each  $R^2$  is a propylene group, b is 0, and p is 0, i.e. when the compound is bis-(gamma-trimethoxysilylpropyl)amine.

These materials may be referred to as disilylated secondary amines used in the present invention may be prepared by processes known in the art for example, as disclosed in US Patent Nos. 2,832,754, 2,920,095 and 5,101,055.

### Multifunctional Acrylates

The multifunctional acrylates of the present invention are defined as acrylates having, on average, greater than two functional acrylate groups per molecule and a molecular weight of from about 100 to about 3000. Multifunctional acrylates are preferred over monofunctional acrylates because monofunctional acrylates do not form flexible, crack free coatings as do the multifunctional acrylates. The majority of multifunctional acrylates commercially available can be used, but it is the smaller, more compact, i.e., proportionally more reactive acrylates that give the best results. The multifunctional acrylates are preferably selected from the group consisting of acrylated polyols with molecular weights of from about 150 to about 600; polyester urethane acrylates with molecular weights of from about 1000 to about 2000; polyether acrylates with molecular weights from 200 to 1500; polyurethane acrylates with molecular weights of from about 400 to about 2000; polyurea acrylates with molecular weights of from about 400 to about 2000; epoxy acrylates with molecular weights of from about 300 to about 1000; and mixtures of multifunctional acrylates thereof.

Most preferred acrylates are pentaerythritol tetraacrylate; an acid functional acrylate; polyester tetra acrylate; polyether tetra acrylate; an aliphatic urethane acrylate, Ebecryl® 1290; ditrimethylolpropane tetra acrylate; an ethoxylated trimethylol propane triacrylate, Ebecryl® 160. Other preferred acrylate include glycerol triacrylate, triacrylate ester of tris-[2-hydroxyethyl] isocyanurate, hexane dioldiacrylate, and dipentaerythritol hexacrylate. Ethoxylated and propoxylated versions of these acrylates may be used in this invention. These acrylates and methods of their production are well known in the art, and available commercially from such

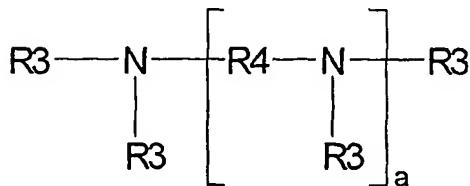
companies as UCB Radcure, (Smyrna, GA) and Sartomer Corp. (Exton, PA). As used herein, the term "mixtures of multifunctional acrylates" means mixtures of different acrylates of the same species, such as two different epoxy acrylates, or mixtures of different species of acrylates, such as epoxy acrylates and urethane acrylates.

### **Ethylenically Unsaturated Acid**

In addition to the bis-silane and the multifunctional acrylate, a quantity of an ethylenically unsaturated acid is added to the composition. By "ethylenically unsaturated acid" it is meant any acid which has vinyl unsaturation. It is believed that the ethylenically unsaturated acid substantially improves the oxygen barrier performance of the composition because the carboxylic group forms an amine salt with amino groups of the bis-silane, which contributes significantly to the coating's barrier properties. The ethylenically unsaturated acid is likely to be added in the amount of at least 5 to about 60 parts by weight of the composition, with about 30 to about 50 parts by weight being most preferred. The most preferred ethylenically unsaturated acids used in the present invention are dicarboxylic (i.e. have two carboxylic acid groups) and the most preferred is itaconic acid; however, other acids such as fumaric, maleic, citraconic, methacrylic, cinnamic, vinyl sulfonic acid, mesaconic acid, and itaconic acid monomethylester may also be used. The term "ethylenically unsaturated acid" as used herein includes mixtures of one or more of the aforementioned acids.

### **Optional Aminofunctional Silanes**

The optional aminofunctional silanes are described generally by the formula:



wherein  $a$  is 0-4, i.e.,  $0 \leq a \leq 4$ ;

$R^3$  is independently hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, arylalkyl, acryl, methacryl, alkylaryl,  $R^4 - SiR_m(OR)_{3-m}$ , or an alkylene linking group having 2 to 12 carbon

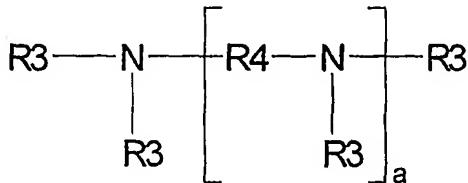
atoms connected to one or two nitrogen atoms, with the proviso that at least one  $R^3$  is a hydrogen

atom and at most one  $R^3$  is an  $R^4 - SiR_m(OR)_{3-m}$  group, where  $m$  is 0, 1 or 2, and R is independently a hydrogen or an alkyl group having from 1 to 6 carbon atoms;

$R^4$  is independently selected from the group consisting of linear or branched alkylene groups having from 1 to 12 carbon atoms; arylene groups having from 6 to 12 carbon atoms; and linear or branched hydrocarbon groups having from 1 to 16 carbon atoms and at least one alcohol, alcohol ether, ester, amide, urea, thiourea or polyether group.

The most preferred optional aminofunctional silanes useful for the present invention are N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, aminopropyltriethoxysilane, and blends thereof.

For the purposes of the present invention, the above mentioned amine functional silane group has the general formula



In the above formula,  $R^3$  is a monovalent radical independently selected from the group consisting of hydrogen; acryl, methacryl, alkyl groups having 1 to 18 carbon atoms, such as methyl, ethyl, propyl, isobutyl, hexyl, octyl, decyl, dodecyl and octadecyl; substituted alkyl having 1 to 18 carbon atoms, such as 3-chloropropyl and 3,3,3-trifluoropropyl; aryl having 6 to

16 carbon atoms, such as phenyl and naphthyl; substituted aryl having 6 to 30 carbon atoms, such as chlorophenyl, chlorotolyl and dichloroxylyl; arylalkyl having 7 to 9 carbon atoms, such as benzyl, phenethyl and 3-phenylpropyl; and alkylaryl having 7 to 16 carbon atoms, such as tolyl, xylyl, ethylphenyl and propyltolyl. According to the invention, at least one R<sup>3</sup> group is hydrogen. Further, at most one R<sup>3</sup> is an R<sup>4</sup> - SiR<sub>m</sub>(OR)<sub>3-m</sub> group, where R is an alkyl group having from 1 to 6 carbon atoms, m is 0, 1, or 2 and R<sup>4</sup> is defined below. The remaining R<sup>3</sup> groups on the aminosilane are preferably hydrogen or methyl.

R<sup>3</sup> can also be an alkylene linking group which links two different nitrogen atoms together, thus forming a cyclic aminosilane. The alkylene linking group can also be an arylene group which is connected to the same nitrogen atom. The alkylene linking group will have at least 2 carbon atoms and as many as 12 carbon atoms.

R<sup>4</sup> is an organic connecting group which provides a separation of at least one carbon atom between the nitrogen atoms or the nitrogen and silicon atoms. Thus, R<sup>4</sup> can be an alkylene group having at least 1 carbon atom or an arylene group having at least 6 carbon atoms. Preferably, R<sup>4</sup> is selected from the group consisting of ethylene, propylene, butylene, isobutylene, trimethylene, tetramethylene, and hexamethylene.

In addition, R<sup>4</sup> can contain polar groups such as, linear or branched hydrocarbon groups having from 1 to 16 carbon atoms and at least one alcohol, alcohol ether, ester, amide, urea, thiourea or polyether group. Specific examples of such groups include, those having the general formula -CH<sub>2</sub>CH(OH)(CH<sub>2</sub>)<sub>x</sub>- , -CH<sub>2</sub>CH(OH)(CH<sub>2</sub>)<sub>x</sub>-O-(CH<sub>2</sub>)<sub>y</sub>- , -CH<sub>2</sub>CH(CH<sub>3</sub>)C(=O)-O-(CH<sub>2</sub>)<sub>y</sub>- , -CH<sub>2</sub>CH<sub>2</sub>C(=O)-O-(CH<sub>2</sub>)<sub>y</sub>- , -CH<sub>2</sub>CH<sub>2</sub>C(=O)-N(R)-(CH<sub>2</sub>)<sub>y</sub>- , -C(=O)-N(R)-(CH<sub>2</sub>)<sub>y</sub>- , -C(=S)-N(R)-(CH<sub>2</sub>)<sub>y</sub>- , or where x and y are each integers from 1 to 12.

The hydroxyl and ester groups are highly polar, and it is believed the polar nature of the groups improve barrier properties.

Examples of specific amine-containing groups include such structures as

-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(H)CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>,

-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(H)CH<sub>2</sub>CH<sub>2</sub>N(H)CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>,

-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(H)Me, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(H)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>,

-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(H)Et, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(Et)H, -CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>N(H)CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> and

-CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>NH<sub>2</sub>, inter alia, wherein Me and Et denote methyl and ethyl, respectively.

A specific example of an amine containing cyclic group is piperazine.

As used herein the term "aminofunctional silane" can mean a single species of the formula described above, such as N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, or it can mean mixtures or one or more species of aminofunctional silanes, such as

N-(2-aminoethyl)-3-aminopropyltrimethoxy silane and aminopropyltriethoxysilane.

The above described aminofunctional silanes can be prepared by methods known to those skilled in the art, and which are amply described in the chemical literature.

### Solvents

The components of the present invention can optionally be reacted together in a solvent. In general, water, alcohols and blends thereof will serve as suitable solvents because the multifunctional acrylate and the ethylenically unsaturated acid are soluble therein. Typically, the solvent is an alcohol. In addition, the selected solvent must wet the substrate. Preferably, the solvent will not extend the drying time of the coating beyond what is commercially acceptable. The amount of solvent can range from about 0% to about 99% and is preferably from about 5% to about 95 parts by weight of the total composition. Preferred solvents are methanol, ethanol, n-propanol, isopropanol, butanol, and 1-methoxy-2-propanol (available as

"Dowanol® PM" from the Dow Chemical Co., Midland, MI).

### Critical Ratios

During the reaction of bis-silanes with multifunctional acrylates, it is possible to utilize an excess of multifunctional acrylate over and above that required to react with the amino nitrogen atoms. In multifunctional acrylates, such as pentaerythritol tetraacrylate, the amine chains attached to the trimethoxysilyl groups may also have pendent acrylate groups which will undergo further polymerization under the influence of ionizing radiation. It is believed that, under the appropriate experimental conditions, the acrylate groups of the multifunctional acrylate and the amino groups of the bis-silane and/or aminofunctional silanes undergo an addition reaction (Michael Addition) upon mixing of these two components. In addition, hydroxyl groups and solvents present may interact with alkoxy groups attached to the silicone atoms of the bis-silanes and/or aminofunctional silane and cause a thickening of the composition at certain concentrations of the components in the solvent.

For example, one may employ an "amine rich" system, in which the total number of amine functional sites in the composition due to the bis-silanes and/or aminofunctional silane can be up to about five (5) times greater than the total number of acrylate sites in the composition due to the multifunctional acrylate, i.e., the ratio of amine functionality to the acrylate functionality can be from about 5:1 to about 1:1, with a ratio of about 3:1 to about 1:1 being preferred, and with a ratio of 1:1:1 being most preferred. In the case where the bis-silane is bis-(gamma-trimethoxysilylpropyl)amine) and the multifunctional acrylate is pentaerythritol tetraacrylate, the ratios in the amine rich system can be expressed in terms of molar ratios, with the preferred molar ratio of bis-silane to multifunctional acrylate being from about 6:1 to about 4:1, with a molar ratio of about 4:1 being most preferred.

Excellent results can also be achieved using an "acrylate rich" system, where the total

number of reactive nitrogen sites in the composition from the bis-silanes is up to about ten (10) times less than the total number of reactive acrylate sites in the composition due to the multifunctional acrylate, i.e., the ratio of amine functionality to acrylate functionality can be from about 1:1 to about 1:10, with a range of about 1:1 to about 1:6 being preferred, and with a ratio of 1:5 being most preferred. In the case where the bis-silane is bis-(gamma-trimethoxysilylpropyl)amine and multifunctional acrylate is pentaerythritol tetraacrylate, the ratios of the acrylate rich system can be expressed in terms of molar ratios, with the preferred molar ratio of aminosilane to multifunctional acrylate being from about 1:1 to about 1:3, with a molar ratio of about 1:1.2 being most preferred.

Although the order of addition of the components is not critical, certain methods are preferable. For example, the bis-silanes and the acrylate component can be added together to form a Michael Adduct, before the addition of the ethylenically unsaturated acid. Also, the ethylenically unsaturated acid may be added at some point after the Michael Addition reaction begins, but before the bis-silanes and/or the acrylate are completely consumed. "Quenching" the reaction by adding the ethylenically unsaturated acid can occur at any point in the reaction process, i.e., the acid may be added to the bis-silanes before any acrylate is added, or after some of the acrylate is added. Practically, the reaction may be quenched at a predetermined point by simply adding part of the acrylate to the bis-silanes, then adding the rest of the acrylate and the acid to this mixture. It is preferred that the quenching technique be used where the acid is first added to the bis-silanes or mixture of bis-silane/aminosilane prior to the addition of any acrylate.

### **Adhesive Thickness**

The adhesive can be applied in any desired amount, however, it is preferred that the adhesive be applied in a thickness ranging from 0.05  $\mu\text{m}$  to 15  $\mu\text{m}$ , the preferred thickness range

being from about 0.5 to about 7  $\mu\text{m}$ . Adhesive thickness can be determined by Scanning Electron Microscopy. The adhesive can be applied to the substrate by any conventional method, such as spray coating, roll coating, slot coating, meniscus coating, immersion coating, and direct, offset, and reverse gravure coating.

### Substrates

The adhesive can be disposed on a wide variety of substrates, including, but not limited to polyolefins, such as oriented polypropylene (OPP), cast polypropylene, polyethylene and polyethylene copolymers, polystyrene, polyesters, such as polyethylene terephthalate (PET), or polyethylene naphthalate (PEN), polyolefin copolymers, such as ethylene vinyl acetate, ethylene acrylic acid and ethylene vinyl alcohol (EVOH), polyvinylalcohol and copolymers thereof, polyamides such as nylon and meta-xylene adipamide (MXD6), polyimides, polyacrylonitrile, polyvinylchloride, polyvinylidene chloride, and polyacrylates, ionomers, polysaccharides, such as regenerated cellulose, and silicone, such as rubbers or sealants, other natural or synthetic rubbers, glassine or clay coated paper, paper board or craft paper, and metallized polymer films and vapor deposited metal oxide coated polymer films, such as  $\text{AlO}_x$ ,  $\text{SiO}_x$ , or  $\text{TiO}_x$ .

The aforesaid substrates are likely to be in the form of a film or sheet, though this is not obligatory. The substrate may be a copolymer, a laminate, a coextrudate, a blend, a coating or a combination of any of the substrates listed above according to the compatibility of the materials with each other. In addition, the substrate may be in the form of a rigid container made from materials such as polyethylene, polypropylene, polystyrene, polyamides, PET, EVOH, or laminates containing such materials.

The aforesaid substrates may also be pretreated prior to coating by corona treatment, plasma treatment, acid treatments and flame treatments, all of which are known in the art.

In addition, the compositions of the present invention can be used for a wide variety of packaging containers, such as pouches, tubes, bottles, vials, bag-in-boxes, stand-up pouches, gable top cartons, thermo-formed trays, brick-packs, boxes, cigarette packs and the like. In addition, the compositions of the present invention may be used as a laminating adhesive.

Of course, the present invention is not limited to just packaging applications, and may be used in any application wherein gas, or aroma barrier properties are desired, such as tires, buoyancy aides, inflatable devices generally, etc.

Any of the foregoing substrates may have a primer or primers applied thereon. The primers are applied to the substrates by methods known in the art such as spray coating, roll-coating, slot coating, meniscus coating, immersion coating, and indirect, offset, and reverse gravure coating. Suitable primers include, but are not limited to carbodiimide, polyethylenimine, and silanes, such as N-(2-aminoethyl)-3-aminopropyltrimethoxy silane and aminopropyltriethoxysilane.

The most preferred laminate structures are (where Si represents the coating composition of this invention), OPP/Si/OPP, OPP/Si/PE, metOPP/Si/OPP, metOPP/Si/PET, metal oxide coated PET/Si/PE, metal oxide coated OPP/Si/PE, metal oxide coated PET/Si/PP, metal oxide coated OPP/Si/PP, and PE/Si/PE.

### Curing

While the compositions of the present invention will form films at ambient conditions, optimum results are achieved by heating and/or free radical cures of the laminate structure.

For example, the first substrate may be exposed to heat and/or moisture prior to lamination of the second substrate. Generally, the higher the temperature, the faster the coating will dry. The upper limit to the drying temperature is the temperature at which the substrate will undergo unacceptable distortion. Also, temperature will accelerate the rate of hydrolysis of

silicon/alkoxy groups and also the rate of condensation of the silicon/alkoxy groups with silicon/hydroxy groups to form silicon-oxygen-silicon groups. The composition may be dried at room temperature or in an oven at temperatures up to about 140°C, with temperatures of from about 60°C to about 120°C being preferred and temperatures of about 90°C to about 110°C being most preferred. Heating time is temperature dependent and the coating will reach tack free time in one to 10 seconds. The heating step serves to evaporate the solvent and accelerate the condensation reaction between Si-OH groups and SiOH/SiOH groups.

The compositions are further cured by initiating a free radical reaction after the second substrate is contacted with the first substrate. The most preferred method of initiating the free radical reaction is through the use of electron beam radiation, although ultraviolet or free radical generators such as azo compounds and peroxides may also be used.

The compositions are preferably cured by a free radical generator, such as ultraviolet, electron beam, or gamma radiation or chemical free radical generators such as azo compounds and peroxides. Low energy electron beam is the preferred method of curing because it is cheaper than gamma sources like Cobalt M-60. Its advantage over ultraviolet radiation as a cure system lies in its ability to generate free radicals without photoinitiators. It also imparts higher yields of crosslink density and chemical grafting of the coating to the substrate. Electron beam accelerators of various types such as van de Graaf-type, resonance transformer-type, linear-type, dynamatron-type and high frequency-type can be used as a source of electron beam. Electron beams having energy of from about 5 to about 2000 KeV, preferably from about 50 to about 300 KeV discharged therefrom may be irradiated in a dose of from about 0.1 to about 30 Mrads (MR). Low electron beam voltages (less than 20 KeV) may be used if the substrate is treated in a vacuum. Commercially available sources of electron beam are Electro Curtain CB-150 available from Energy Sciences, Inc. (Wilmington, MA).

The compositions may also be ultraviolet light cured if one or more photoinitiators is added prior to curing. There are no special restrictions on the photoinitiators as long as they can generate radicals by the absorption of optical energy. Ultraviolet light sensitive photoinitiators or blends of initiators used in the UV cure of the present composition include 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocure 1173), sold by EM Chemicals, and 2,2 Dimethoxy-2-phenyl-acetol-phenone (Irgacure 651), sold by Ciba-Geigy Corporation, Hawthorne, New York. For purposes of this invention, it has been found that from about 0.05 to about 5 weight percent based on the total solids in the composition, of the photoinitiators described therein will cause the composition to cure.

In addition to radical polymerization and grafting to crosslink the coating after it has been applied to the film substrate, it is possible to further crosslink the amine silane materials utilizing acid catalyzed condensation reactions. In this reaction, a methoxylated active hydrogen compound, such as trimethylol phenol, or a mixture of formaldehyde with aldehydes, ketones, and other active hydrogen compounds react with amine salts, such as the itaconate salts of the amine silanes or derivatives to form alkylated amines.

### Preferred Embodiments

To prepare the preferred embodiment of the invention, the bis-silane component, preferably bis-(gamma-trimethoxysilylpropyl)amine (4 g) is dissolved in a solvent such as methanol. Itaconic acid (2 g) is added to this solution. This mixture is allowed to equilibrate for one hour. The acrylate, preferably pentaerythritol tetraacrylate (PETA) (2 g), is added to the above solution and the mixture is allowed to equilibrate for 15 hours at ambient conditions. The coating solution is applied to corona treated 30  $\mu\text{m}$  thick oriented polypropylene film from UCB Films (product # T217/30) and the coated film is allowed to dry under ambient conditions for 20 minutes. Another piece of corona treated OPP film is placed on top of the dried coating and the

composite is passed through a hot roll laminator (Chem Instruments HL 101 Hot Roll Laminator) set at 60°C. This laminated material is then "cured" by an electron beam dose of 10 Megarads at 165 Kv.

### **Optional Additives**

Various optional additives can be added to the composition to improve various properties. These additives may be added as desired and in any amount as long as they do not degrade the performance of the barrier coatings as illustrated herein. Examples of additives include additional additives as earlier described, antiblock and slip aides such as stearamide oleamide or polar additives, such as epoxides, polyols, glycidols or polyamines, such as polyethylenimine, and other silanes such as N-(2-aminoethyl)-3-aminopropyltrimethoxy silane and aminopropyltriethoxysilane may also be added. Wetting agents, such as a polyethoxylated alkyl phenol may also be added.

### **Examples**

Experiments 1-4 -- A1170 & bis-TMSEDA addition to/replacement of Z6020 in Z6020/PETA/ITA (50:25:25wt) formulation (EB Cure)

The (Z6020/bis-silane)/PETA:ITA formulations were utilized in a weight ratio of 50:25:25 with a total solids content of 8 grams/20 grams of solution. The solvent employed in all the experiments described below was methanol. The N-(2-amino ethyl)gamma aminopropyl trimethoxysilane (Z-6020) was obtained from Dow Corning Corporation (Midland, MI), the bis-( $\gamma$ -trimethoxysilylpropyl)amine (A1170) from Witco, the bis-[ $(3$ -trimethoxysilyl)propyl]ethylenediamine (62% solution in MeOH) (TMSEDA) from Gelest, the pentaerythritol tetraacrylate (PETA) from Sartomer and the itaconic acid (ITA) from Acros Chemicals. The coating solutions were all applied to corona treated 30  $\mu\text{m}$  thick "Rayopp" oriented polypropylene film from UCB Films utilizing a #18 Myer rod. The coated film was allowed to dry under ambient conditions for 20 minutes. Another piece of corona

treated OPP film was placed on top of the dried coating and the composite was passed through a hot roll laminator (Chem Instruments HL 101 Hot Roll Laminator) set at 60°C. This laminated material was then "cured" by an EB machine at 10 Megarads and 165 Kv.

The oxygen permeability values for each film herein were measured and recorded in units of cc/square meter per 24 hours, "dry" values being measured at 0% relative humidity and "wet" values at 90% relative humidity utilizing MOCON Oxtran 2/20 Series. Some of the laminates were also evaluated at 80% RH. The MOCON instruments were obtained from Modern Controls Corporation. For comparison, the polypropylene base film had a permeability of about 1200 cc/square meter/24 hours. The adhesive layer thickness was measured by means of Scanning Electron Microscopy (SEM).

Experiment 1 -- Z6020/PETA/ITA 50:25:25wt

ITA (2g) was added to a solution of Z6020 (4g) in methanol (12g) and the resulting mixture stirred for 30 mins. The acrylate (PETA, 2g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 3.6cc dry, and 507.2cc wet and the adhesive layer thickness was determined to be 2.2  $\mu\text{m}$ .

Experiment 2 -- Z6020/A1170/PETA/ITA 25:25:25:25wt

ITA (2g) was added to a solution of Z6020 (2g) and A1170 (2g) in methanol (12g) and the resulting mixture stirred for 30 mins. The acrylate (PETA, 2g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 3.4cc dry, 145cc at 80%RH and 279.2cc wet and the adhesive layer thickness was determined to be 2.4  $\mu\text{m}$ .

Experiment 3 -- A1170/PETA/ITA 50:25:25wt

ITA (2g) was added to a solution of A1170 (4g) in methanol (12g) and the resulting mixture stirred for 30mins. The acrylate (PETA, 2g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 15.3cc dry, 81.3cc at 80%RH and 154.8cc wet and the adhesive layer thickness was determined to be 4.5 $\mu$ m.

Experiment 4 -- bis-TMSEDA/PETA/ITA 50:25:25wt

ITA (2g) was added to a solution of bis-TMSEDA (6.45g) in methanol (9.55g) and the resulting mixture stirred for 30mins. The acrylate (PETA, 2g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 8.09cc dry, 61.9cc at 80%RH and 155cc wet and the adhesive layer thickness was determined to be 3.6  $\mu$ m.

The barrier data for experiments 1 - 4 is summarized below in Table 1.

Table 1

Expt #	bis-silane type	Weight Ratio Z6020/bis-silane/PETA/ITA	OTR <sup>1</sup>	OTR	OTR	OTR predicted <sup>2</sup>	OTR predicted <sup>3</sup>	OTR predicted <sup>4</sup>
			90%RH cc/m <sup>2</sup> /day	80%RH cc/m <sup>2</sup> /day	0% RH cc/m <sup>2</sup> /day	3 μm adhesive 90%RH μm cc/m <sup>2</sup> /day	3 μm adhesive 80%RH cc/m <sup>2</sup> /day	3 μm adhesive 0%RH cc/m <sup>2</sup> /day
1	none	50:0:25:25	507.2	450	3.6	2.2	417.6	364.6
2	A1170	25:25:25:25	279.2	145	3.4	2.4	233.9	118.7
3	A1170	0:50:25:25	154.8	81.2	15.3	4.5	218.5	118.1
4	bis-TMSEDA	0:50:25:25	155	61.9	8.09	3.6	181.5	73.6
								9.7

In Table 1, the following abbreviations and meanings are used, wherein:

1: OTR is oxygen transmission rate or oxygen gas permeability

2: OTR <sub>predicted</sub> was calculated by the use of the Generic Composite Permeability Eqt:

$T_t/P_t = T_s/P_s + T_c/P_c$  where T refers to the thickness, in microns, and P to the permeability coefficient of the composite ( $T_t, P_t$ ), substrate( $T_s, P_s$ ), & adhesive ( $T_c, P_c$ ). The substrate OPP was measured to be 30 microns thick and have an OTR of 1238cc/m<sup>2</sup>/day as measured at 90%RH.

3: same as 2 except that the permeability was measured to be 1266 cc/m<sup>2</sup>/day at 80%RH

4: same as 2 except that the permeability was measured to be 1191 cc/m<sup>2</sup>/day at 0%RH  
Experiments 5-7 -- A1170 & bis-TMSEDA replacement of Z6020 in Z6020/PETA/ITA (20:49:31wt) formulation (EB Cure)

In experiments 5-7 the (Z6020/bis-silane)/PETA:ITA formulations were utilized in a weight ratio of 20:49:31 with a total solids content of 8 grams/20 grams of solution. The solvent employed in all the experiments described below was methanol. The Z6020 was obtained from Dow Corning Corporation (Midland, MI), the Silquest A1170 from Witco, the TMSEDA from Gelest, the PETA from Sartomer and the itaconic acid from Acros Chemicals. The coating solutions were all applied to corona treated 30 µm thick "Rayopp" oriented polypropylene film from UCB Films utilizing a #18 Myer rod. The coated film was allowed to dry under ambient conditions for 20 minutes. Another piece of corona treated OPP film was placed on top of the dried coating and the composite was passed through a hot roll laminator (Chem Instruments HL 101 Hot Roll Laminator) set at 60°C. This laminated material was then "cured" by an EB machine at 10Megarads and 165Kv.

Experiment 5 -- Z6020/PETA/ITA 20:49:31wt

ITA (2.48g) was added to a solution of Z6020 (1.6g) in methanol (12g) and the resulting mixture stirred for 30mins. The acrylate (PETA, 3.92g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 36.9cc dry, 58.4cc at 80%RH and 105.7cc wet and the adhesive layer thickness was determined to be 2.66  $\mu\text{m}$ .

Experiment 6 -- A1170/PETA/ITA 20:49:31wt

ITA (2.48g) was added to a solution of A1170 (1.6g) in methanol (12g) and the resulting mixture stirred for 30mins. The acrylate (PETA, 3.92g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 34.6cc dry, 74.2cc at 80%RH and 112.8cc wet and the adhesive layer thickness was determined to be 2.1  $\mu\text{m}$ .

Experiment 7 -- bisTMSEDA/PETA/ITA 20:49:31wt

ITA (2.48g) was added to a solution of bisTMSEDA (2.58g) in methanol (11.02g) and the resulting mixture stirred for 30mins. The acrylate (PETA, 3.92g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 25.4cc dry and 44.4cc wet and the adhesive layer thickness was determined to be 2.2  $\mu\text{m}$ .

The barrier data for experiments 5 - 7 is summarized in Table 2.

Table 2

Expt #	bis-silane type	Weight Ratio Z6020/bis-silane/PETA/TTA	OTR <sup>1</sup>		Adhesive Thickness $\mu\text{m}$	OTR predicted <sup>2</sup>		OTR predicted <sup>3</sup> 3 $\mu\text{m}$ adhesive 80%RH $\text{cc}/\text{m}^2/\text{day}$	OTR predicted <sup>4</sup> 3 $\mu\text{m}$ adhesive 0%RH $\text{cc}/\text{m}^2/\text{day}$
			90%RH $\text{cc}/\text{m}^2/\text{day}$	80%RH $\text{cc}/\text{m}^2/\text{day}$		3 $\mu\text{m}$ adhesive 90%RH $\text{cc}/\text{m}^2/\text{day}$	3 $\mu\text{m}$ adhesive 80%RH $\text{cc}/\text{m}^2/\text{day}$		
5	none	20:0:49:31	105.7	58.4	36.9	2.66	94.6	52.1	32.8
6	A1170	0:20:49:31	112.8	74.2	34.6	2.1	81.2	52.9	24.4
7	bis-TMSEDA	0:20:49:31	44.4	-	25.4	2.2	32.9	-	18.7

Experiments 8-10 -- A1170 & bis-TMSEDA replacement of Z6020 in Z6020/PETA/ITA (50:30:20wt) formulation (EB Cure)

In experiments 8-10 the (Z6020/bis-silane)/PETA:ITA formulations were utilized in a weight ratio of 50:30:20 with a total solids content of 8 grams/20 grams of solution. The solvent employed in all the experiments described below was methanol. The Z6020 was obtained from Dow Corning Corporation (Midland, MI), the Silquest A1170 from Witco, the TMSEDA from Gelest, the PETA from Sartomer and the itaconic acid from Acros Chemicals. The coating solutions were all applied to corona treated 30  $\mu\text{m}$  thick "Rayopp" oriented polypropylene film from UCB Films utilizing a #18 Myer rod. The coated film was allowed to dry under ambient conditions for 20 minutes. Another piece of corona treated OPP film was placed on top of the dried coating and the composite was passed through a hot roll laminator (Chem Instruments HL 101 Hot Roll Laminator) set at 60°C. This laminated material was then "cured" by an EB machine at 10Megarads and 165Kv.

Experiment 8 -- Z6020/PETA/ITA 50:30:20wt

ITA (1.6g) was added to a solution of Z6020 (4g) in methanol (12g) and the resulting mixture stirred for 30mins. The acrylate (PETA, 2.4g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 4.5cc dry and 547.6cc wet and the adhesive layer thickness was determined to be 2.5  $\mu\text{m}$ .

Experiment 9 -- A1170/PETA/ITA 50:30:20wt

ITA (1.6g) was added to a solution of A1170 (4g) in methanol (12g) and the resulting mixture stirred for 30mins. The acrylate (PETA, 2.4g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 27.9cc dry and 210.5cc wet and the adhesive layer thickness was determined to be 2.6  $\mu\text{m}$ .

Experiment 10 -- bisTMSEDA/PETA/ITA 50:30:20wt

ITA (1.6g) was added to a solution of bisTMSEDA (6.45g) in methanol (9.55g) and the resulting mixture stirred for 30mins. The acrylate (PETA, 2.4g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 20.9cc dry and 218cc wet and the adhesive layer thickness was determined to be 2.0  $\mu\text{m}$ .

The barrier data for experiments 8 - 10 are summarized in Table 3 below.

Table 3

Expt #	bis-silane type	Weight Ratio Z6020/bis-silane/PETA /ITA	OTR <sup>1</sup>	Adhesive Thickness	OTR predicted <sup>2</sup>	OTR predicted <sup>3</sup>
			90% RH cc/m <sup>2</sup> /day	μm	3 μm adhesive 90% RH cc/m <sup>2</sup> /day	3 μm adhesive 0% RH cc/m <sup>2</sup> /day
8	none	50:0:30:20	547.6	4.5	2.5	492.7 3.8
9	A1170	0:50:30:20	210.5	27.9	2.6	186.7 24.3
10	bis-TMSED A	0:50:30:20	218	20.9	2.0	154.4 14

Experiments 11-13 -- A1170 & bis-TMSEDA replacement of Z6020 in Z6020/PETA/ITA (50:20:30wt) formulation (EB Cure)

In experiments 11-13 the (Z6020/bis-silane)/PETA:ITA formulations were utilized in a  
5 weight ratio of 50:20:30 with a total solids content of 8 grams/20 grams of solution. The solvent employed in all the experiments described below was methanol. The Z6020 was obtained from Dow Corning Corporation (Midland, MI), the Silquest A1170 from Witco, the TMSEDA from Gelest, the PETA from Sartomer and the itaconic acid from Acros Chemicals.  
The coating solutions were all applied to corona treated 30  $\mu\text{m}$  thick "Rayopp" oriented  
10 polypropylene film from UCB Films utilizing a #18 Myer rod. The coated film was allowed to dry under ambient conditions for 20minutes. Another piece of corona treated OPP film was placed on top of the dried coating and the composite was passed through a hot roll laminator (Chem Instruments HL 101 Hot Roll Laminator) set at 60°C. This laminated material was then "cured" by an EB machine at 10Megarads and 165Kv.

15 Experiment 11 -- Z6020/PETA/ITA 50:20:30wt

ITA (2.4g) was added to a solution of Z6020 (4g) in methanol (12g) and the resulting mixture stirred for 30mins. The acrylate (PETA, 1.6g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 1.2cc dry and  
20 468.9cc wet and the adhesive layer thickness was determined to be 2.1  $\mu\text{m}$ .

Experiment 12 -- A1170/PETA/ITA 50:20:30wt

ITA (2.4g) was added to a solution of A1170 (4g) in methanol (12g) and the resulting mixture stirred for 30mins. The acrylate (PETA, 1.6g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After  
25 coating, drying, laminating and curing, the permeability was determined to be 12.3cc dry and 254cc wet and the adhesive layer thickness was determined to be 3.0  $\mu\text{m}$ .

## Experiment 13 -- bisTMSEDA/PETA/ITA 50:20:30wt

ITA (2.4g) was added to a solution of bisTMSEDA (6.45g) in methanol (9.55g) and the resulting mixture stirred for 30 minutes. The acrylate (PETA, 1.6g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 5.4cc dry and 176.7cc wet and the adhesive layer thickness was determined to be 2.6  $\mu\text{m}$ .

The barrier data for experiments 11 - 13 is summarized in Table 4 below.

Table 4

Expt #	bis-silane type	Weight Ratio Z6020/bis-silane/PETA/ITA	OTR <sup>1</sup>		Adhesive Thickness μm	OTR predicted 2		OTR predicted 3 3 μm adhesive 90% RH cc/m <sup>2</sup> /day
			90% RH cc/m <sup>2</sup> /day	0% RH cc/m <sup>2</sup> /day		3 μm adhesive 90% RH cc/m <sup>2</sup> /day	3 μm adhesive 0% RH cc/m <sup>2</sup> /day	
11	none	50:0:20:30	468.9	1.2	2.1	370.3	0.8	
12	A1170	0:50:20:30	254	12.3	3.0	254	12.3	
13	bis-TMSEDA	0:50:20:30	176.7	5.4	2.6	156.1	4.7	

Experiments 14-17 -- A1170 & bis-TMSEDA addition to/replacement of Z6020 in Z6020/PETA/ITA (34:46:20wt) formulation (EB Cure)

In experiments 14-17 the (Z6020/bis-silane)/PETA:ITA formulations were utilized in a  
5 weight ratio of 34:46:20 with a total solids content of 8 grams/20 grams of solution. The solvent employed in all the experiments described below was methanol. The Z6020 was obtained from Dow Corning Corporation (Midland, MI), the Silquest A1170 from Witco, the TMSEDA from Gelest, the PETA from Sartomer and the itaconic acid from Acros Chemicals. The coating solutions were all applied to corona treated 30  $\mu\text{m}$  thick "Rayopp" oriented  
10 polypropylene film from UCB Films utilizing a #18 Myer rod. The coated film was allowed to dry under ambient conditions for 20 minutes. Another piece of corona treated OPP film was placed on top of the dried coating and the composite was passed through a hot roll laminator (Chem Instruments HL 101 Hot Roll Laminator) set at 60°C. This laminated material was then "cured" by an EB machine at 10Megarads and 165Kv.

15 Experiment 14 -- Z6020/PETA/ITA 34:46:20wt

ITA (1.6g) was added to a solution of Z6020 (2.72g) in methanol (12g) and the resulting mixture stirred for 30 minutes. The acrylate (PETA, 3.68g) was added to this solution and the resulting mixture was used 3 hours after making because it gelled when stirred for greater than 8 hours. This solution was used to coat the plastic film. After coating, drying,  
20 laminating and curing, the permeability was determined to be 16.7cc dry and 231.3cc wet and the adhesive layer thickness was determined to be 2.5  $\mu\text{m}$ .

Experiment 15 -- Z6020/A1170/PETA/ITA 17:17:46:20wt

ITA (1.6g) was added to a solution of Z6020 (1.36g) and A1170 (1.36g) in methanol (12g) and the resulting mixture stirred for 30 minutes. The acrylate (PETA, 3.68g)  
25 was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was

determined to be 40.7cc dry and 253.3cc wet and the adhesive layer thickness was determined to be 2.9  $\mu\text{m}$ .

Experiment 16 -- A1170/PETA/ITA 34:46:20wt

ITA (1.6g) was added to a solution of A1170 (2.72g) in methanol (12g) and the  
5 resulting mixture stirred for 30 minutes. The acrylate (PETA, 3.68g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 140.9cc dry and 231.8cc wet and the adhesive layer thickness was determined to be 3.0  $\mu\text{m}$ .

Experiment 17 -- bis-TMSEDA/PETA/ITA 34:46:20wt

10 ITA (1.6g) was added to a solution of bis-TMSEDA (4.39g) in methanol (10.33g) and the resulting mixture stirred for 30 minutes. The acrylate (PETA, 3.68g) was added to this solution and the resulting mixture was stirred for 15 hours. This solution was used to coat the plastic film. After coating, drying, laminating and curing, the permeability was determined to be 91.9cc dry and 228.3cc wet and the adhesive layer thickness was determined to be 2.6  $\mu\text{m}$ .

15 The barrier data for experiments 14 - 16 is summarized in Table 5 below.

Table 5

Expt #	bis-silane type	Weight Ratio Z6020/bis-silane/PETA/ITA	OTR <sup>1</sup>		Adhesive Thickness $\mu\text{m}$	OTR predicted 2		OTR predicted 3 3 $\mu\text{m}$ adhesive 0% RH $\text{cc}/\text{m}^2/\text{day}$
			90% RH $\text{cc}/\text{m}^2/\text{day}$	0% RH $\text{cc}/\text{m}^2/\text{day}$		90% RH $\text{cc}/\text{m}^2/\text{day}$	0% RH $\text{cc}/\text{m}^2/\text{day}$	
14	none	34:0:46:20	231.3	16.7	2.5	198.9	13.9	
15	A1170	17:17:46:20	253.3	40.7	2.9	246.5	39.4	
16	A1170	0:34:46:20	231.8	140.9	3.0	231.8	140.9	
17	bis-TMSEDA	0:34:46:20	228.3	91.9	2.6	202.8	80.5	

Other variations may be made in compounds, compositions, and methods described herein without departing from the essential features of the invention. The embodiments of the invention specifically illustrated herein are exemplary only and not intended as limitations on their scope except as defined in the appended claims.

## Claims:

1. A method of laminating two substrates comprising:

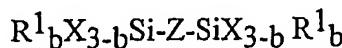
(i) coating at least one side of a substrate with a laminating adhesive,

(ii) bringing a coated side of said substrate into contact with a second substrate to form a multi-layer film, and

(iii) treating said multi-layer film with a free radical initiator,

wherein said laminating adhesive is the reaction product of a multifunctional acrylate, a bis-silane, an optional aminofunctional silane, and an ethylenically unsaturated acid, optionally dissolved in a solvent,

10 wherein the multifunctional acrylate has a molecular weight of from 100 to 3000, and the bis-silane has at least one molecule of the formula

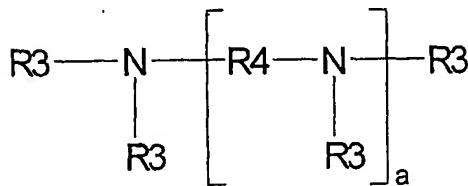


wherein Z is  $R^2NH(R^2NH)p R^2$ , each  $R^1$  is a hydrocarbon group, each X is an alkoxy group

with 1 to 4 carbon atoms, a halogen atom, an oxime group or an acyloxy group, each  $R^2$  is a

15 divalent hydrocarbon group having 1 to 12 carbon atoms; b is from 0 to 3 and p is 0 or 1; and

the optional aminofunctional silane has the formula



wherein a is 0-4;

$R^3$  is independently hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, arylalkyl,

20 acryl, methacryl, alkylaryl,  $R^4 - SiR_m(OR)_{3-m}$ , or an alkylene linking group having 2 to 12

carbon atoms connected to one or two nitrogen atoms, with the proviso that at least one  $R^3$  is a

hydrogen atom and at most one R<sup>3</sup> is an R<sup>4</sup> - SiR<sub>m</sub>(OR)<sub>3-m</sub> group, where m is 0, 1 or 2, and R is independently a hydrogen or an alkyl group having from 1 to 6 carbon atoms; and

R<sup>4</sup> is independently selected from the group consisting of linear or branched alkylene groups having from 1 to 12 carbon atoms; arylene groups having from 6 to 12 carbon atoms; 5 and linear or branched hydrocarbon groups having from 1 to 16 carbon atoms and at least one alcohol, alcohol ether, ester, amide, urea, thiourea or polyether group.

2. The method of claim 1, wherein there is a total amine functionality and a total acrylate functionality and the ratio of amine functionality of the bis-silane to the acrylate functionality of the multifunctional acrylate is from 1:1 to 1:6.

10 3. The method of claim 1, wherein the reaction product is dissolved in a solvent and the solvent is a water/alcohol mixture where the alcohol present in an amount of 1-100% and the solvent constitutes 5-95 parts by weight of the total composition.

4. The method of claim 1, wherein said free radical reaction is initiated by electron beam radiation, gamma radiation or ultraviolet radiation, optionally in the presence of photoinitiators, 15 or said free radical reaction is initiated thermally in the presence of a free radical generator.

5. The method of claim 1, wherein the coated substrate of step (II) is heated in the presence of moisture.

6. The method of claim 1, wherein the substrate is selected from the group consisting of 20 polyolefins, including oriented polypropylene (OPP), cast polypropylene, polyethylene and polyethylene copolymer; polystyrene; polyesters, including polyethylene terephthalate (PET), or polyethylene naphthalate (PEN); polyolefin copolymers, including ethylene vinyl acetate, ethylene acrylic acid and ethylene vinyl alcohol (EVOH), polyvinylalcohol and copolymers thereof; polyamides including nylon and meta-xylene adipamide (MXD6); polyimides;

polyacrylonitrile; polyvinylchloride; polyvinyl dichloride; polyvinylidene chloride; polyacrylates; ionomers; polysaccharides, including regenerated cellulose; silicone, including rubbers or sealants; natural or synthetic rubbers; glassine or clay coated paper; paper board; craft paper; and metallized films and vapor deposited metal oxide coated polymer films, including

5       $\text{AlO}_x$ ,  $\text{SiO}_x$ , or  $\text{TiO}_x$ .

7. The method of claim 14, wherein the laminate is deposited on one or more additional substrates to form a laminate, and said additional substrate or substrates are optionally primed.

8. The method of claim 1, wherein the second substrate is selected from the group consisting of polyolefins, including oriented polypropylene (OPP), cast polypropylene, 10 polyethylene and polyethylene copolymer; polystyrene; polyesters, including polyethylene terephthalate (PET), or polyethylene naphthalate (PEN); polyolefin copolymers, including ethylene vinyl acetate, ethylene acrylic acid and ethylene vinyl alcohol (EVOH), polyvinylalcohol and copolymers thereof; polyamides including nylon and meta-xylene adipamide (MXD6); polyimides polyimides; polyacrylonitrile; polyvinylchloride; polyvinyl dichloride; polyvinylidene chloride; polyacrylates; ionomers; polysaccharides, including 15 regenerated cellulose; silicone, including rubbers or sealants; natural or synthetic rubbers; glassine or clay coated paper; paper board; craft paper; and metallized films and vapor deposited metal oxide coated polymer films, including  $\text{AlO}_x$ ,  $\text{SiO}_x$ , or  $\text{TiO}_x$ .

9. The method of claim 1, wherein the reaction product of step (I) includes an additive, 20 and said additive is selected from the group consisting of a silane, polyethylenimine, glycidyl methacrylate, glycidol, ethylene glycol diglycol ether, bisphenol A, polyethoxylated phenol.

10. The method of claim 1, wherein the substrate of step (II) is primed with a primer selected from the group consisting of a silane, polyethylenimine, and carbodiimide.

11. A composition made by the method of claims 1-10.
12. A packaging container, the improvement comprising a laminate film integral therewith, the laminate formed by the method of claim 1.
  13. The packaging container of claim 12, wherein the package is selected from the group consisting of a pouch, tube, vial, bottle, bag-in-box, stand-up pouch, gable top carton, thermoformed tray, brick-pack, box, and cigarette pack.